

**PHYSICAL RESEARCH ON
LIQUID-METAL SYSTEMS**

**Annual Report
July 1975—June 1976**

by

**V. A. Maroni, W. F. Calaway, E. Veleckis,
R. M. Yonco, F. A. Cafasso, and L. Burris**

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Printed in the United States of America
Available from
National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22161
Price: Printed Copy \$4.00; Microfiche \$3.00

ANL-76-106

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

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Chemical Engineering Division

Previous reports in this series

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ANL-75-50 July 1974—June 1975

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CHEMICAL ENGINEERING DIVISION
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ABSTRACT

Physicochemical and thermodynamic studies of liquid-lithium-containing systems have continued. Pressure-composition isotherms for the Li-H system measured by a gravimetric technique are found to be in reasonably good agreement with earlier tensimetric results. Plateau-pressure studies of the Li-H, Li-D, and Li-T systems have been made at temperatures above and below the monotectic. The observed isotope effects were found to be near the predicted values. Measurements of the solubility of LiD in liquid lithium gave results in good agreement with prior data for the solubility of LiH in lithium and confirmed that the limits on cold trapping of lithium hydrides from lithium are too high for projected fusion reactor applications. Determination of the solubility of Li_2O in liquid lithium is nearing completion. Solubility values measured to date are slightly lower than, but in the range of, prior measurements.

SUMMARY

Gravimetric Studies of Hydrogen-Liquid Metal Systems

Studies are continuing in an effort to determine pressure-composition-temperature data for hydrogen and deuterium in lithium-containing liquid metal systems by a gravimetric technique. Experiments were performed to determine variation of the plateau pressure with temperature for the Li-H system in the range from 700 to 800°C as a check on the previous temperature calibration of the system. Results obtained with the gravimetric apparatus agree to within $\pm 0.5\%$ with accepted values. Pressure-composition isotherms have been measured at 793 and 745°C. These results are presented and compared with tensimetric results in the full report.

Plateau Pressure Studies of the Li-H, Li-D and Li-T Systems

Previous work on the Li-H and Li-D systems has suggested that the bulk of the D/H isotope effect can be accounted for by the differences in the decomposition pressures over the Li-H and Li-D solutions. In order to determine the H/D/T isotope effects, additional tensimetric measurements were made on the systems Li-H, Li-D, and Li-T while maintaining the alloy concentrations within the miscibility gap limits, where the decomposition pressures stay on a constant "plateau." The results indicate that, for a given temperature, the plateau pressures tend to increase with increasing isotopic mass.

The values of P_{D_2}/P_{H_2} and P_{T_2}/P_{H_2} are very near the corresponding square root mass ratios ($\sqrt{2}$ for D/H and $\sqrt{3}$ for T/H). The data were also used in establishing the monotectic temperature for each system (694°C for Li-H, 690°C for Li-D, and 688°C for Li-T).

Solubility of Lithium Deuteride in Liquid Lithium

Knowledge of the solubility of hydrogen isotopes in liquid lithium is important in selecting methods for their recovery from fusion reactor blankets. We measured the solubility of deuterium by taking equilibrated melt samples from saturated solutions of deuterium in lithium and assaying them for deuterium. The results obtained from twelve melt samples show that the solubility decreases from 21.4 mol % LiD at the monotectic temperature (690°C) to 0.035 mol % LiD at the eutectic temperature (180.3°C). Relatively high solubility near the eutectic appears to rule out those methods of hydrogen isotope separation from lithium that are based on cold-trapping concepts. The solubility data were treated to produce analytical equations for the activity coefficients and for the liquidus curve. Our data agree well with recent measurements of the solubility of hydrogen in lithium by electrical resistance methods.

Solubility of Lithium Oxide in Liquid Lithium

The solubility of lithium oxide in liquid lithium is being measured by a direct sampling technique in which filtered samples of saturated solutions are taken at various temperatures and are analyzed for oxygen by a fast-neutron activation method. Sampling of the solutions has been completed (28 samples over a temperature range from 195 to 734°C), but analysis of the samples is still in progress. Preliminary estimates appear to indicate that our final solubility values will be somewhat lower and will have a better correlation coefficient than those previously reported in the literature.

I. INTRODUCTION

The physical research described in this report is directed toward gaining a better understanding of the solution chemistry of nonmetals in liquid lithium. This area of research has pertinence in controlled thermonuclear research and electrochemical battery research. Previous progress reports in the series covering this work are given in Refs. 1-4. Reported below are results of (1) gravimetric studies of hydrogen solutions in liquid lithium; (2) plateau pressure studies of the Li-H, Li-D, and Li-T systems; (3) investigations of the solubility of lithium deuteride in liquid lithium; and (4) measurements of the solubility of lithium oxide in liquid lithium.

II. GRAVIMETRIC STUDIES OF HYDROGEN-LIQUID METAL SYSTEMS (J. B. Kiefer* and W. F. Calaway)

Studies are continuing in an effort to measure pressure-composition isotherms for hydrogen and deuterium in lithium-containing liquid metal systems by a gravimetric technique.^{1,4} The objective of this program is the development of an experimental method for rapid data acquisition on liquid metal-hydrogen systems by accelerating equilibration between gaseous hydrogen and liquid metal samples that are sealed in capsules permeable to hydrogen. Gravimetric methods have been found to meet this criterion in that the hydrogen pressure can be easily and quickly varied to increase the rate of diffusion through the capsule walls. In order to determine the reliability of the gravimetric technique, experiments are being conducted on the Li-H system for which pressure-composition isotherms are well established.⁵

As discussed previously,¹ temperature measurements of the samples are not straightforward and calibration curves for the purpose of correcting the measured temperatures are required. As a check on the accuracy of these corrections, experiments were performed to determine the plateau pressure for the Li-LiH system as a function of temperature in the range from 700 to 800°C. Results were found to agree with those obtained from tensimetric experiments in which somewhat more direct temperature measurements could be made.⁵ Based on the plateau pressure equation for the Li-LiH system from Ref. 5, results obtained with the gravimetric apparatus indicate discrepancies in the corrected temperature measurement of $\sim 0.5\%$. Although this is a small uncertainty, it corresponds to an absolute error of $\pm 4^\circ\text{C}$ at 800°C. Furthermore, temperature variations of a few degrees introduce considerable error into the pressure-composition data for the Li-H

The experimental apparatus presently in use has been described elsewhere.^{1,4} A sealed niobium-1% zirconium capsule containing liquid lithium is attached to an automatic recording vacuum microbalance and suspended inside a heated hang-down tube. Hydrogen gas at a pressure of ~ 500 torr is introduced into the hang-down tube in order to drive the hydrogen into the sample capsule by permeation. As the hydride composition of interest is approached, the hydrogen pressure is reduced and varied until equilibrium is reached between the Li-LiH solution and the external hydrogen pressure. When equilibrium is attained, the weight of the sample capsule, the pressure

*ANL Undergraduate Research Program Participant from Moorehead State University.

of the hydrogen, and the temperature of the sample are recorded. The measured weight gain of the capsule is due to (1) formation of LiH , (2) thermomolecular flow (TMF) effects on the balance, and (3) hydrogen uptake by the capsule. Correction factors accounting for the latter two effects are obtained by performing the hydridation experiments on an empty capsule. These correction factors are used in conjunction with the observed experimental weight gains and the total weight of the lithium in the capsule to calculate the mole fraction of lithium hydride formed at each pressure and temperature measured.

Results for isotherms at 793°C and 745°C are given in Fig. 1, together with the pressure-composition isotherms calculated from the tensimetric data.⁵

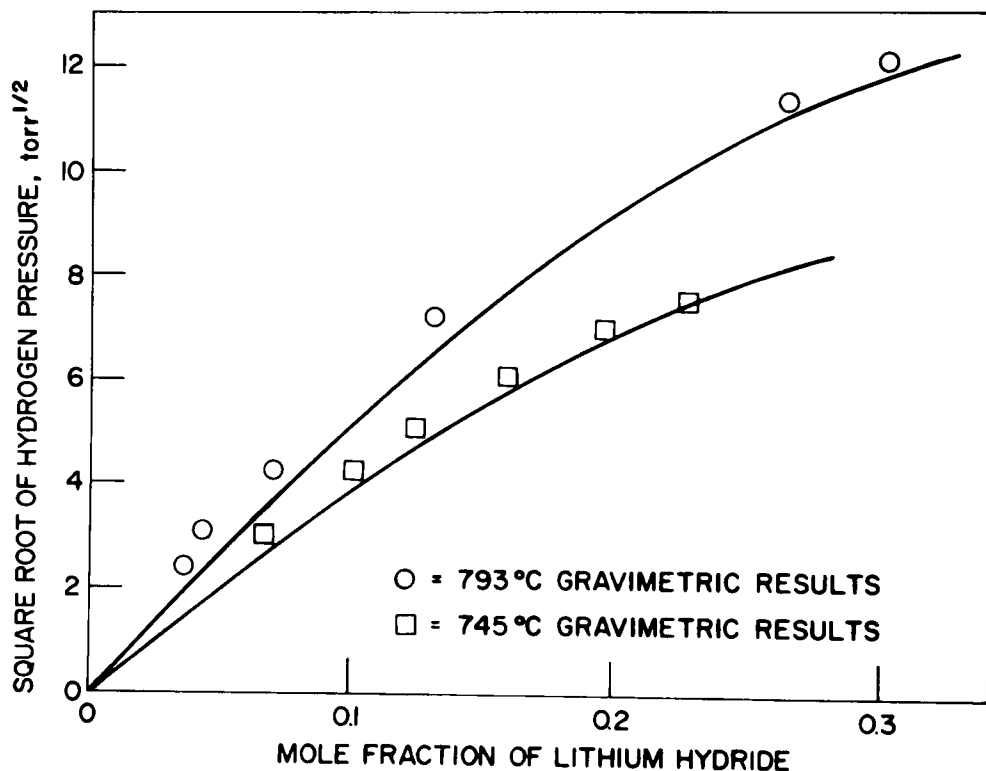


Fig. 1. Comparison of Gravimetric and Tensimetric Results for 745 and 793°C . Solid lines represent calculated data from tensimetric results; squares and circles represent gravimetric results at 745 and 793°C , respectively.

The discrepancies between the two sets of data can be attributed to two problems associated with the gravimetric experiment. Part of this discrepancy is the uncertainty, discussed earlier, in measuring the temperature of the capsule. Another factor appears to be a loss of lithium from the capsule; *i.e.*, throughout the experiment, there was a downward drift in the weight of the sample capsule of ~ 1.5 mg/day. (A slight discoloration was observed at the neck of the capsule and on the quartz hang-down tube. Soon after the experiment, the neck of the capsule broke off, again lending support to the

supposition that lithium was leaking out at that point. If the total amount of lithium in the capsule is less than originally thought, then the data points would be shifted to higher lithium hydride mole fractions and would thus be in better agreement with the tensimetric results.)

The development of the gravimetric technique is continuing. In principle, this method should provide a fast and reliable means for studying liquid metal-hydrogen systems. The experimental difficulties that have hindered a demonstration of the full potential of the gravimetric technique in this application are presently being resolved. Also, other lithium-containing systems (such as Li-Pb-H) should be more suited to the present equipment than the Li-H system since they are less sensitive to small temperature and pressure variations.

III. PLATEAU PRESSURE STUDIES OF THE Li-H, Li-D AND Li-T SYSTEMS (E. Veleckis)

Previous work on the Li-H⁵ and Li-D⁶ system has suggested that the bulk of the D/H isotope effect is accounted for by the differences in the decomposition pressures over the Li-H and Li-D solutions. In order to determine more precisely the H/D and H/T isotope effects, additional tensimetric measurements were made on the systems Li-H, Li-D, and Li-T, using improved experimental conditions. The improvements were accomplished by (1) limiting the alloy concentrations to values within the miscibility-gap limits, where the decomposition pressures do not vary with composition; (2) miniaturizing the lithium sample and apparatus to allow study of the Li-T system; and (3) maintaining identical experimental procedures for each system.

Plateau pressures were measured as follows. Approximately 35 mg of lithium was sealed in a small iron capsule having sufficiently thin walls to permit rapid permeation of hydrogen, deuterium, or tritium. The encapsulated lithium was reacted with ~40 std. cm³ of gas (H₂, D₂ or T₂) to produce an ~60 mol % LiH, LiD, or LiT solution. Equilibrium decomposition pressures were then measured in 25-degree intervals between 600 and 800°C.

The results are listed in Table 1 and are shown graphically in Fig. 2, where the logarithms of the plateau pressures are plotted against 1/T. The "as received" tritium used in this work was found* to contain only 89.62 mol % of total T₂, the balance being 1.62 mol % total D₂ and 8.76 mol % total H₂. Plateau pressures obtained for this mixture were corrected to correspond to pure tritium, assuming conformity to Raoult's law by the LiH, LiD, and LiT species in the condensed phase. A brief description of the method used in calculating the corrections is given in the Appendix.

Each plot in Fig. 2 has two distinct linear segments, the crossing point of which represents the monotectic temperature for the corresponding system (694°C for Li-H, 690°C for Li-D, and 688°C for Li-T). The coefficients of the linear equations derived for each segment are listed in Table 2.

*The tritium analyses were performed at Mound Laboratory, Miamisburg, Ohio.

Table 1. Plateau Pressures of the Li-H, Li-D, and Li-T Systems

Li-H		Li-D		Li-T		
Temp, °C	P _{H₂} , torr	Temp, °C	P _{D₂} , torr	Temp, °C	P _{T₂} (obs), torr	P _{T₂} (corr), torr
858.3	380.9	850.6	461.2	844.4	442.8	461.4
841.2	300.1	827.5	337.7	820.0	314.2	327.9
839.6	295.8	799.7	225.6	792.2	211.6	221.4
820.3	223.8	774.5	155.0	767.6	147.7	155.1
818.9	217.8	762.1	127.1	742.2	99.0	104.3
800.0	166.8	751.6	109.9	732.7	85.7	90.53
785.4	129.2	738.7	88.15	720.7	67.7	71.27
768.8	100.6	726.9	71.10	710.7	57.4	60.51
755.5	81.0	712.3	56.50	694.0	44.0	46.70
743.1	65.7	702.3	47.40			
731.5	54.2	692.0	38.78	680.5	32.5	34.66
718.5	43.8			667.6	22.9	24.39
716.7	42.2	677.5	27.37	659.9	18.9	20.17
704.6	34.1	666.4	20.64	647.6	13.3	14.16
		653.1	13.94	636.4	9.58	10.17
693.5	27.6	641.9	10.35	621.1	6.36	6.79
682.9	20.8	627.7	7.00	616.6	5.55	5.92
669.5	14.96			611.0	4.64	4.94
657.3	10.76			595.8	3.06	3.28
647.4	7.97					
630.6	5.16					

As is seen in Fig. 2, for a given temperature, the plateau pressures tend to increase with increasing isotopic mass. This finding is consistent with expectation because, in the progression from hydride to tritide, the heats of formation increase, whereas the entropies of formation decrease (Table 2). The observed isotope effects are listed in Table 3 for several temperatures. At lower temperatures, the values of P_{D_2}/P_{H_2} and P_{T_2}/P_{H_2} are near the corresponding square root of mass ratios ($\sqrt{2}$ for D/H and $\sqrt{3}$ for T/H). At temperatures above the monotectic, however, the isotope effects tend to decrease slightly, reflecting trends in the regression coefficients (Table 2).

Combined with existing pressure-composition-temperature data for the Li-rich region of the Li-T phase diagram,⁷ our plateau-pressure data for tritium will be used to derive thermodynamic information for the regions of homogeneous solution outside the miscibility gap. In addition, because the isotope effects are expected to remain essentially constant throughout the entire composition range, the results of this study should be useful in evaluating hydrogen-isotope separation methods based on distillation concepts.

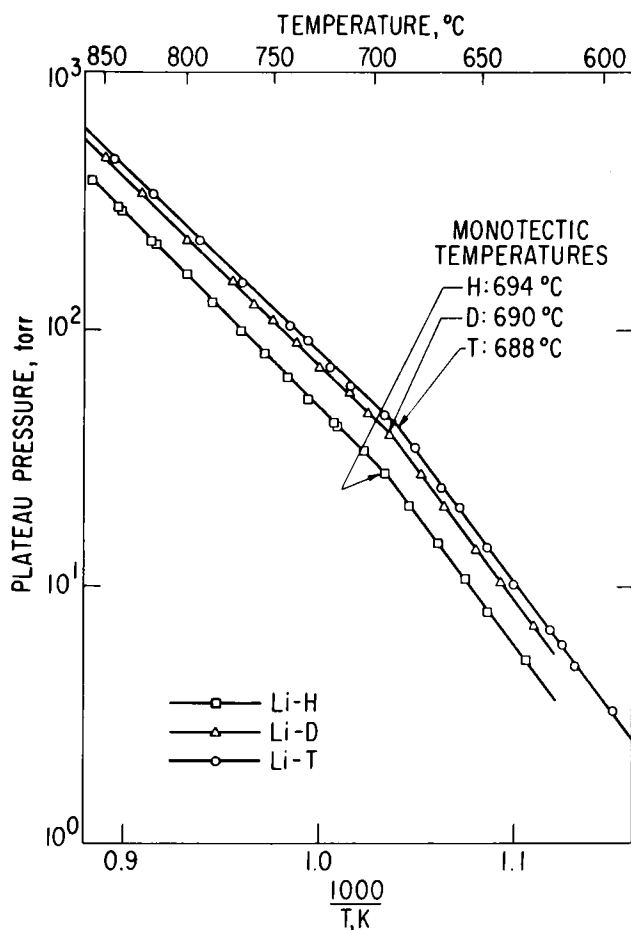


Fig. 2. Plateau Pressure Data for the Li-H, Li-D, and Li-T Systems

Table 2. Monotectic Temperatures and Regression Coefficients for the Li-H, Li-D, and Li-T Systems. (Regression lines are represented by $\ln P(\text{torr}) = A + BT^{-1}$ where P is the plateau pressure and T is the temperature in kelvins.)

System	Monotectic Temperature, °C	Below Monotectic		Above Monotectic	
		A	B	A	B
Li-H	694	27.50	-23,380	21.34	-17,420
Li-D	690	28.13	-23,590	21.15	-16,880
Li-T ^a	688	27.87	-23,220	20.92	-16,530

^aCalculated from the $P_{T_2}(\text{corr})$ values of Table 1.

Table 3. Temperature Dependence of
D/H and T/H Isotope Effects

Temperature, °C	P_{D_2}/P_{H_2} (± 0.03)	P_{T_2}/P_{H_2} (± 0.03)
600	1.46	1.75
650	1.48	1.73
700	1.45	1.65
750	1.42	1.57
800	1.38	1.51
850	1.35	1.45

IV. SOLUBILITY OF LITHIUM DEUTERIDE IN LIQUID LITHIUM (E. Veleckis and R. M. Yonco)

An ongoing effort in our physical research program is the determination of the solubility of hydrogen isotopes in liquid lithium. The liquidus curves of the Li-LiH and Li-LiD systems are only partially known. Above the monotectic temperatures (694°C for Li-LiH and 690°C for Li-LiD), the lines have been determined in our previous studies.^{5,6} Below the monotectic, however, virtually no data were available until recently, when studies of the solubility of hydrogen⁸ and deuterium⁹ in liquid lithium, using electrical resistance methods, were reported by workers at the University of Nottingham. Concurrently, we initiated an investigation to measure the solubility of deuterium in lithium between 220 and 500°C by a direct sampling method which consisted of taking equilibrated melt samples from saturated solutions of deuterium in lithium and then assaying them for deuterium.

Solubility measurements were made using the same apparatus and experimental approach as that employed for the Li-Li₃N system.^{1,10} Briefly, the procedure was as follows. Approximately 250 g of pure lithium was placed in an Armco iron vessel which was attached to the bottom of a helium-atmosphere glove box. A Li-5.5 mol % LiD mixture was prepared *in situ* by reacting the molten lithium with a measured volume (~22.5 std. liters) of pure deuterium. Samples of the melt were taken by lowering pre-evacuated, fritted nickel sample tubes into the melt and then pressurizing the melt with helium. The deuterium content in the samples was determined by individually sealing the filled sample tubes in Armco iron capsules, heating them to 840°C, collecting the thermally decomposed deuterium with a Toepler pump, and measuring the volume of the evolved gas. The composition of the gas was then determined by a mass-spectrometric analysis.

Solubility data for 12 equilibrated melt samples collected between 199 and 498°C are listed in Table 4, together with the previously reported¹ solubilities at and above the monotectic temperature.

Figure 3 shows a plot of 1000 K/T vs. log solubility. The plot is constructed in this manner in order to resemble conventional phase diagrams with expanded low-temperature scales. Owing to the large deviations from

TABLE 4. Mole-Fraction Concentration and Activity Coefficient of LiD Along the Liquidus Line of the Li-LiD System.

Temperature, °C	N'_{LiD} ^b	γ'_{LiD} ^{b,c}
199	0.000514	270
221	0.000768	200
246	0.00122	141
272	0.00181	107
304	0.00322	69.8
323	0.00427	57.7
351	0.00633	44.1
375	0.00866	35.9
397	0.0114	30.0
397	0.0117	29.3
451	0.0208	20.7
498	0.0332	15.6
690 ^a	0.214	4.60
705	0.228	4.33
756	0.279	3.54
805	0.333	2.94
840	0.374	2.58
871	0.413	2.31

^aMonotectic temperature.

^bAt and above the monotectic, the values of N'_{LiD} and γ'_{LiD} were taken from Ref. 6.

^cBelow the monotectic, each γ'_{LiD} was calculated from the corresponding N'_{LiD} using Eq. 1.

ideality of the Li-LiD solutions, the solubility data in Fig. 3 do not fall on a straight line. A smooth liquidus curve connecting the data points was generated in the manner described below.

Consider a solution having a composition that corresponds to the liquidus curve at the monotectic temperature (21.4 mol % LiD). At this point $a_{\text{LiD}} \approx 1$ and, therefore, the monotectic temperature may be looked upon as the freezing point of pure LiD ("solvent"). As more Li ("solute") is added, the solution will undergo a freezing point lowering, as shown in Fig. 3 by the descending branch of the solubility curve. The activity of the saturated solvent, a'_{LiD} ,

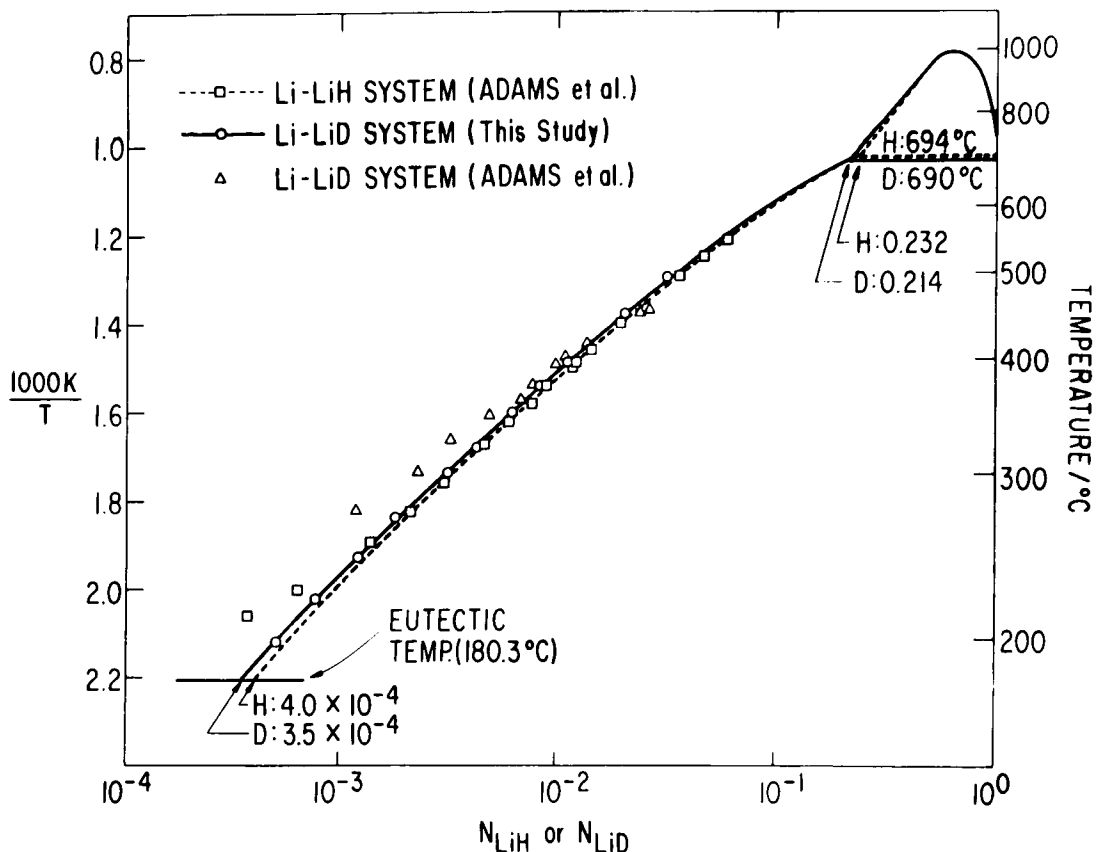


Fig. 3. Phase Diagrams for the Li-LiH and Li-LiD Systems
Projected on the Plane 1000 K/T vs. Log Composition

may be related to the freezing point lowering by the equation¹¹

$$\begin{aligned} \ln a'_{\text{LiD}} &= \ln \gamma'_{\text{LiD}} N'_{\text{LiD}} \\ &= \ln a^{\circ}_{\text{LiD}} - \frac{\Delta H_f}{R} \frac{\theta}{TT_f} + \frac{\Delta a}{R} \left[\frac{\theta}{T} + \ln \left(1 - \frac{\theta}{T_f} \right) \right] + \frac{\Delta b}{R} \frac{\theta^2}{2T} \end{aligned} \quad (1)$$

where the primed symbols refer to saturated solutions; γ'_{LiD} and N'_{LiD} are, respectively, the activity coefficient and the mole fraction of LiD at the liquidus line; H_f is the latent heat of fusion of LiD¹²; T_f is the monotectic temperature; $\theta = (T_f - T)$ is the freezing point lowering; $\Delta C_p = \Delta a + \Delta bT$ is the difference between the heat capacities of liquid and solid LiD;¹² and $a^{\circ}_{\text{LiD}} = 0.984$ is the activity of LiD at the monotectic temperature and serves here as the standard state for liquid LiD.

Equation 1 was used to calculate activity coefficients for points below the monotectic temperature. At and above this temperature, the γ'_{LiD} values were taken from our previous work⁶ (see Table 4).

It is customary to express the activity coefficients of a binary solution in terms of a power series in N . Applied to the Li-LiD solutions, and with the series truncated at the cubic term, one obtains $\ln \gamma_{\text{LiD}} = \alpha N_{\text{Li}}^2 + \beta N_{\text{Li}}^3$. Assuming α and β to be linear functions of $1/T$, this analytical form was used to fit the activity coefficient data in Table 4, giving the equation

$$\frac{\ln \gamma_{\text{LiD}}}{N_{\text{Li}}^2} = (1.124 - 2.776 N_{\text{Li}}) + (1/T)(3,285 + 143.8 N_{\text{Li}}) \quad (2)$$

which represents the γ'_{LiD} data within $\pm 2\%$. Omission of primes indicates that Eq. 2 is applicable (in the range 199–871°C) throughout the entire homogeneity range of the Li-rich region ($0 < N_{\text{LiD}} < N'_{\text{LiD}}$).

Simultaneous solution of Eqs. 1 and 2 yields an expression that relates deuteride solubility to temperature. Thus,

$$\begin{aligned} \ln N'_{\text{LiD}} - 10.372 \ln T + 4.8314 \times 10^{-3} T + (67.917 + 591.35 T^{-1}) \\ + (6.0800 - 7,001.4 T^{-1}) N'_{\text{LiD}} - (7.2040 - 3,716.4 T^{-1}) N'^2_{\text{LiD}} \\ + (2.7760 - 143.80 T^{-1}) N'^3_{\text{LiD}} = 0 \end{aligned} \quad (3)$$

Numerical solution of Eq. 3 generated the liquidus curve, shown in Fig. 3, between the monotectic and eutectic temperatures. The same treatment was applied to the electrical resistance data for the Li-LiH system.⁸ The results (shown in Fig. 3) are in good agreement with our Li-LiD data, the hydrogen solubilities being somewhat higher, as expected, owing to H/D isotope effects. The electrical resistance data reported for the Li-LiD system⁹ suggest much lower deuterium solubilities and appear to be inconsistent with the data shown in Fig. 3. A probable cause for these lower values may be the presence of appreciable quantities of residual deuterium in lithium prior to deuteration, due to incomplete degassing.

Data on the solubility of hydrogen isotopes in liquid lithium near its melting point are of interest in assessing the feasibility of cold-trapping tritium in fusion-reactor blankets. Evaluation of Eq. 3 at the melting point of lithium (180.5°C) gives a eutectic composition of 0.035 mol % LiD. This high value appears to rule out the separation of hydrogen isotopes from lithium by cold-trapping methods. The freezing point depression, calculated from the eutectic composition and the latent heat of fusion of lithium (717 cal/mol), was found to be 0.20°C. This gives 180.3°C for the eutectic temperature.

V. SOLUBILITY OF LITHIUM OXIDE IN LIQUID LITHIUM (R. M. Yonco)

A comprehensive program is currently in progress to determine thermodynamic and physicochemical properties of lithium-nonmetallic element binary systems. As a part of this program, we are currently measuring the solubility of lithium oxide in liquid lithium. The Li-Li₂O system had been studied previously by Hoffman¹³ and by Konovalov *et al.*,¹⁴ however, the rather poor agreement among their data (Fig. 4) justifies a more definitive examination of the system. Moreover, the information gained in this work can be applied to the design and analysis of fusion reactor systems, as has been discussed previously.^{4,10,15}

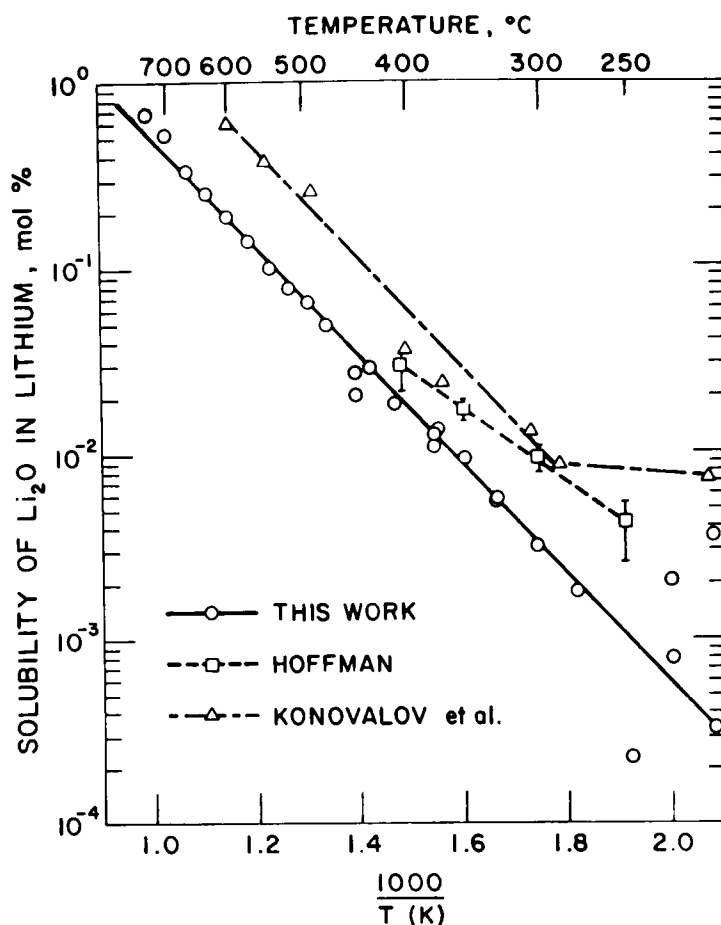


Fig. 4. Solubility of Li_2O in Liquid Lithium

A direct sampling technique is being used in which filtered samples of saturated solutions of Li_2O in liquid lithium are taken in sample tubes having negligible (or, at least, predictable) oxygen contents. The entire content of the sample tube is analyzed for oxygen by a fast-neutron activation method.¹⁶ In this way, errors due to sample segregation or to contamination by oxygen or water are minimized.

The experimental apparatus, shown in Fig. 5, consists of an Armco iron pot designed to hold the saturated solution of lithium oxide in lithium, with provisions made for stirring, sampling, and measuring the temperature of the melt. The furnace pot opens into a helium-atmosphere glove box that is maintained at less than 1 ppm oxygen and water vapor. A solution of lithium oxide in lithium was formed by the direct reaction of lithium metal (204 g of dross-free, low-sodium-grade lithium) with sufficient oxygen (99.994% pure Matheson research grade) to form a 2.5 mol % solution.

The sample tube (Fig. 6) is designed (1) to have the finest porosity filter (2 μm) that will pass liquid lithium under the conditions of the experiment, thereby minimizing the entry of undissolved Li_2O fines into the

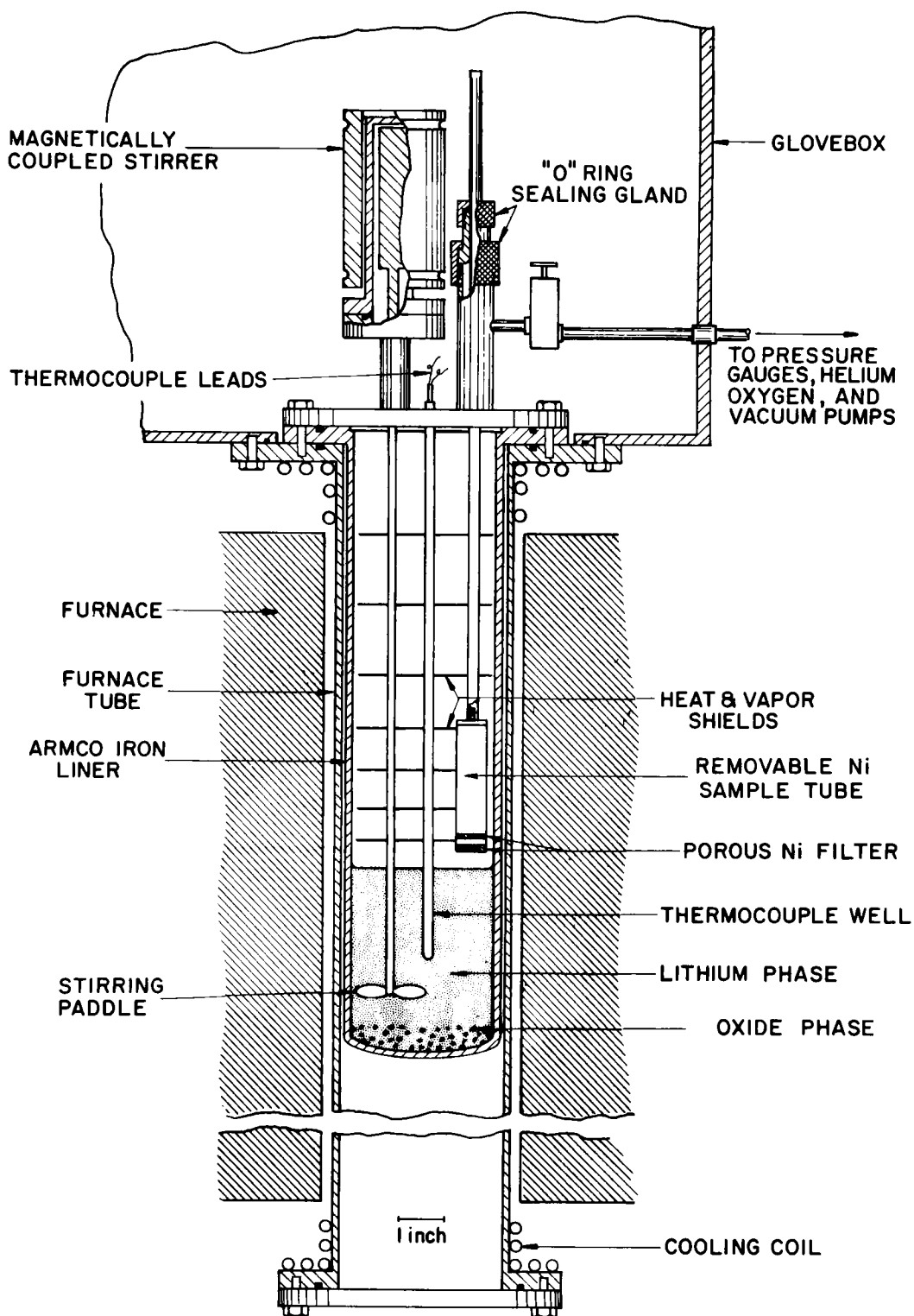


Fig. 5. Apparatus for Measuring the Solubility of Lithium Oxide in Liquid Lithium

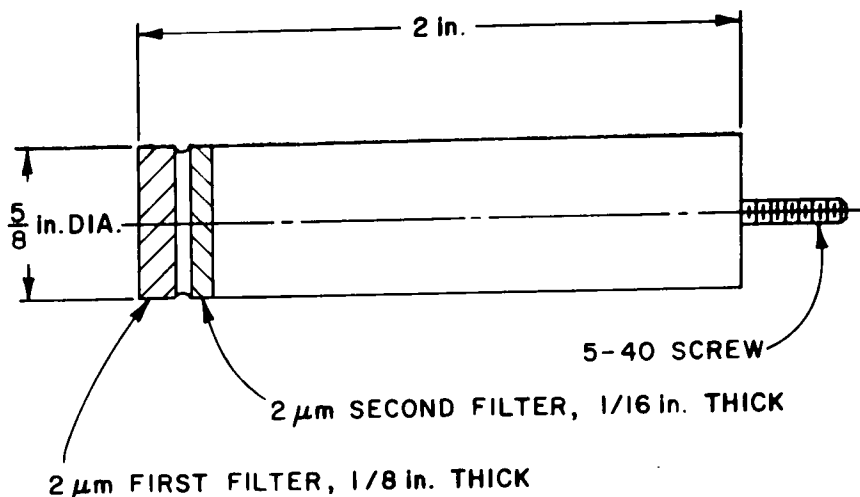


Fig. 6. Sample Tube for Taking Filtered Samples of Saturated Solutions

sample chamber (Hoffman and Konovalov *et al.* used 20 μ m and 30–40 μ m filters, respectively), (2) to have a well-defined oxygen content to permit an accurate blank to be subtracted from the oxygen analysis, and (3) to present the entire sample for analysis, thereby eliminating errors due to sample segregation. The tubes were made of nickel because of the ease with which nickel can be deoxidized by a hydrogen firing procedure; the procedure used consisted of heating the sample tubes to 950°C under an atmosphere of hydrogen gas at 1100 torr.

The lithium oxide solution was brought to equilibrium by stirring for at least 2 hr at a selected temperature. Samples were taken by preheating a sample tube in the furnace, reducing the pressure to 1 torr, immersing the tube in the melt, pressurizing to \sim 1200 torr (with helium), and withdrawing the filled tube from the furnace. Excess lithium was carefully washed from the outside of the sample tube with water, 3% HCl, and alcohol; the tube was then returned to the helium glove box where the first filter was cut off and discarded. Each sample, contained in its truncated sample tube, was sealed in a Pyrex tube with Apiezon W wax and shipped to ORNL for oxygen analysis by a fast-neutron activation method.¹⁶ The samples were then returned to this laboratory, where they were analyzed for lithium, iron, and carbon.

Ten unused hydrogen-fired sample tubes were also analyzed for oxygen and were found to have an average oxygen content of 0.397 ± 0.037 mg. The oxygen blank in the truncated sample tube is then the product of the fraction of the tube remaining with the sample (about 60%) and the oxygen content of the whole tube. For samples that were taken above 300°C, where the total oxygen detected was >0.8 mg, the oxygen blank was calculated from the average value of the oxygen content of a whole tube. Below 300°C, the samples were taken in the previously analyzed sample tubes and the oxygen blanks were calculated from the actual oxygen content found in each tube.

Twenty-eight samples have been taken between 195 and 734°C and, to date, most of these samples have been analyzed for oxygen. Concentrations based on estimated sample weights have been calculated for these samples and are plotted as $\log (\text{mol } \% \text{Li}_2\text{O})$ vs. $1/T$ in Fig. 4.

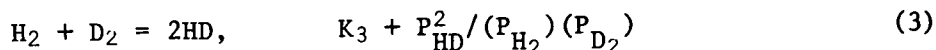
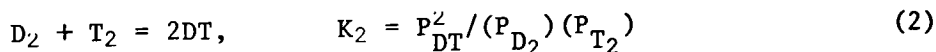
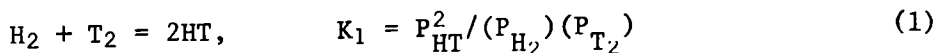
Since these experiments are not yet completed, only tentative solubility values are reported herein. A linear least squares fit of the data for each of the existing data sets (ours, Hoffman's, and that of Konovalov *et al.*) is shown in Fig. 4. Data points below 275°C were omitted from our work and from that of Konovalov *et al.* because the abrupt departure of these points from a straight line has no physical justification in terms of the equilibrium between solid, isomorphic lithium oxide, and liquid lithium. Our data in this region will be examined for possible systematic errors.

Keeping in mind the provisional status of our data, it appears at this point that our solubility values will be generally lower than those previously reported,^{13,14} and that the correlation coefficient for our data will be better than that of the previous investigators. Both factors appear to reflect the apparent success of our efforts in protecting the samples from contamination by air, moisture, and solid inclusions of Li_2O .

APPENDIX

CALCULATIONAL METHOD FOR
PLATEAU-PRESSURE CORRECTIONS

The correction method used in Section III is based on knowledge of the isotopic composition of the gas phase which is assumed to be composed of the species H_2 , D_2 , T_2 , HD , HT , and DT , whose partial pressures are governed by the following equilibria



where P_i is the partial pressure of the i th species in the gas phase and the K 's are known ¹⁷ equilibrium constants.

The condensed phase is a quarternary system, $Li-LiH-LiD-LiT$. Since the constitutions of the binary axes-- $Li-LiH$, $Li-LiD$, and $Li-LiT$ --are very similar, the system may be described in terms of a ternary $LiH-LiD-LiT$ system. Furthermore, it is assumed that each component in this system obeys Raoult's law, *i.e.*,

$$P_{H_2} = (1 - \theta - \omega)^2 P_{H_2}^* \quad (4)$$

$$P_{D_2} = \theta^2 P_{D_2}^* \quad (5)$$

$$P_{T_2} = \omega^2 P_{T_2}^* \quad (6)$$

where θ and ω are, respectively, the mole fractions of LiD and LiT in the $LiH-LiD-LiT$ mixture. $P_{H_2}^*$, $P_{D_2}^*$ and $P_{T_2}^*$ are the equilibrium pressures of H_2 , D_2 , and T_2 for the conditions $\theta = \omega = 0$, $\theta = 1$, and $\omega = 1$, respectively. Numerical values of $P_{H_2}^*$ and $P_{D_2}^*$ can be calculated from the coefficients given in Table 2.

For the gas phase, one can formulate three independent equations relating the partial pressures, *i.e.*,

$$P = P_{H_2} + P_{D_2} + P_{T_2} + P_{HD} + P_{HT} + P_{DT} \quad (7)$$

$$y_D P = P_{D_2} + 1/2 P_{HD} + 1/2 P_{DT} \quad (8)$$

$$y_T P = P_{T_2} + 1/2 P_{HT} + 1/2 P_{DT} \quad (9)$$

where P is the total pressure in the gas phase, and where $y_D = 0.0162$ and $y_T = 0.8962$ are, respectively, the mole fractions of total deuterium and

tritium in the gas phase. Substitution of Eqs. 1-6 into Eqs. 7-9 gives

$$r = (1 - \theta - \omega)^2 + \omega^2 r_T + \theta^2 r_D + \omega(1 - \theta - \omega) \sqrt{K_1 r_T} \\ + \omega \theta \sqrt{K_2 r_D r_T} + \theta(1 - \theta - \omega) \sqrt{K_3 r_T} \quad (10)$$

$$y_D r = \theta^2 r_D + 1/2 \theta \omega \sqrt{K_2 r_D r_T} + 1/2 \theta(1 - \theta - \omega) \sqrt{K_3 r_T} \quad (11)$$

$$y_T r = \omega^2 r_T + 1/2 \omega(1 - \theta - \omega) \sqrt{K_1 r_T} + 1/2 \omega \theta \sqrt{K_2 r_D r_T} \quad (12)$$

where $r = P/P_{H_2}^*$, $r_D = P_{D_2}^*/P_{H_2}^*$, $r_T = P_{T_2}^*/P_{H_2}^*$. Equations 10-12 were solved simultaneously for the unknowns (θ , ω , and r_T) as functions of temperature by the Newton-Raphson iteration method. The resulting values of $P_{T_2}^*$ are given in column 7 of Table 1 (Section III).

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